DISLOCATIONS AND CRYSTAL STRUCTURE*

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INTRODUCTION

The application of X-ray diffraction methods to the study of the internal atomic structure of solids has revealed that almost all solids are crystalline. They consist of a regular periodic arrangement of atoms, or a group of atoms, in three dimensions. This is true even of such solids as plastic, hair and wool. The exact arrangement of atoms inside a solid material is called its crystal structure, and most chemical compounds normally crystallize into definite crystal structures, each with a definite symmetry, unit cell, and number of formula units per cell. Thus sodium chloride, whether obtained from the sea or prepared in the laboratory or found as a mineral, has always shown the same arrangement of sodium and chlorine atoms at the same distance from each other. But there are some substances which crystallize into more than one structure and this property is called polymorphism. A classical example is that of calcium carbonate, which as the mineral Iceland Spar was the subject of much study because of its striking property of double refraction. The formation of two images of an object when viewed at an angle to the trigonal axis of the rhombohedral cell could not be satisfactorily explained on the basis of Newton's corpuscular theory of light, whereas, on the basis of Huygens's wave theory of light the phenomenon could be well understood. Aragonite, another mineral with the same chemical formula, did not show this property because of the different spatial relationship of the carbonate groups in the orthorhombic unit cell. To the chemist the two modifications are one and the same substance, $CaCO_3$; but to the crystallographer they are two different crystals with different structures and different physical properties; for example calcite with a rhombohedral uniaxial crystal has a density $d = 2.71$ gms/cc while aragonite, an orthorhombic biaxial crystal, has a density $d = 2.94$ gms/cc.

POLYMORPHISM

Polymorphism, i.e., the ability the of same chemical compound to exist in more than one crystalline form, was an unexpected phenomenon and its discovery dates back to 1798 when Klaproth studied calcite and aragonite minerals. This observation was contrary to all the accepted ideas of that time. Only after the

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publication of the classical papers of Mitscherlich (1822, 1823) on the arsenates and phosphates and on sulphur, was it accepted beyond doubt that the same chemical compound can exist in more than one crystalline form. Since then a very large number of substances have been discovered to be polymorphic and the transitions between their polymorphic forms have been studied in details. Table 1 lists the known polymorphic forms of a few substances.

TABLE 1. Polymorphic forms of different substances.

	Element or compound	Chemical composition	Known polymorphic forms
1.	Cesium chloride	CsCl	(i) cubic (CsCl type) (s), d=3.64 (ii) cubic (NaCl type) (m), d=3.54
2.	Calcium carbonate	$CaCO_3$	(i) calcite (s), rhombohedral, uniaxial, d=2.71 (ii) aragonite (m), orthorhombic, biaxial, d=2.94
3.	Carbon	C	(i) diamond (m), cubic, very hard, d=3.5, covalent tetrahedral binding, poor conductor. (ii) graphite (s), hexagonal, soft, d=2.2, layer structure good conductor.
4.	Iron	Fe	(i) iron(m), f.c.c. (ii) iron(s) and iron(m). b.c.c.
5.	Mercuric iodide	HgI_2	(i) red (s), tetragonal (ii) yellow (m), orthorhombic
6.	Phosphorus	P_4	(i) white phosphorus(m), d=1.8 ; melts 44°C (ii) violet phosphorus (s), d=2.35 ; melts around 600°C ("red" phosphorus is a solid solution of white in violet)
7.	Silica	SiO_2	(i) quartz(s) (α and β forms) ; d=2.655 (ii) tridymite(m) (α and β forms) ; d=2.27 (iii) cristobalite (m) (α and β forms) ; d=2.30
8.	Sulphur	S	(i) α, orthorhombic (s), d=2.05, melts 113°C (ii) β, monoclinic (m), d=1.93, melts 120°C
9.	Tin	Sn	(i) white tin, tetragonal, d=7.286 stable above 18°C (ii) gray tin, cubic (diamond type), d=5.80, metastable above 18°C (iii) "rhombic" tin (m), orthorhombic, d=6.56
10.	Zinc sulphide	ZnS	(i) wurtzite (m), hexagonal (ii) sphalerite (s), cubic (diamond type)

d=density (gms/cc) ; m=metastable and s=stable, at ordinary temperature and pressure.

THERMODYNAMICAL INTERPRETATION OF POLYMORPHISM

The first definite understanding of polymorphism emerged with the development of thermodynamics towards the end of nineteenth century, when the

polymorphic modifications came to be regarded as different phases of a compound. The phase theory of polymorphism, which developed as a consequence, explained the occurrence of different polymorphic modifications of a compound in terms of their relative thermodynamic stabilities, the one with the least Gibbs free energy being the most stable under any given condition of temperature and pressure. Any particular phase would thus have a definite range of temperature and pressure in which it would be most stable, so that the substance would tend to exist in this phase within this range, and to undergo a phase transition beyond it. Polymorphic transitions in solids were, from this point of view, completely analogous to changes of state.

The application of Clausius—Clapeyron equation and the Gibbs phase rule to polymorphic equilibria drew attention to the effect of pressure on polymorphic transitions as well as the effect of solvents in accelerating transformations. There followed a series of precise experimental studies on polymorphic behaviour of different substances over wide ranges of temperature and pressure. In fa majority of substances have been found to undergo structural transformations when subjected to extremes of temperature and pressure. For example sodium chloride undergoes a polymorphic transition to cesium chloride type of structure when subjected to a pressure of 18000 kg/cm^2 (Endokimova and Vereschagin, 1962). Similarly, transformation of graphite form of carbon to diamond under a pressure of 55,000 to 100,000 kg/cm^2 and a temperature of 1200° to 2400°C in the presence of catalysts like Cr, Mn, Co, Ni, Pd, Pt and Fe_2O_3 has been achieved (Bovenkork *et al* 1959). A vast majority of substances which are not polymorphic at ordinary pressures and temperatures undergo polymorphic transitions under high pressures and temperature. Thus polymorphism is a far more general phenomenon than it had been believed to be.

The phase theory of polymorphism could not however explain the common appearance of metastable states in solids and the different speeds of polymorphic transitions. An understanding of these required the knowledge of the energy barrier opposing such transitions. This energy barrier would depend upon the change of bonding involved in the transformation of the structure. This requires the knowledge of detailed atomic structure which could come about only comparatively recently after the development of X-ray diffraction techniques of structure determination. The structural aspect of polymorphism is able to explain qualitatively the wide range of velocity of transition.

POLYTYPISM

As a result of X-ray investigations, recently a special kind of one dimensional polymorphism, called polytypism has been discovered. This property has been exhibited by certain close-packed and layered structures like silicon carbide, zinc sulphide, cadmium iodide etc. These substances crystallize into a large

number of modifications, all of which are built up by stacking idential unit layers, of structure on top of each other at regular intervals. There are a large number of ways in which these layers can be stacked on top of each other keeping the nearest neighbour relationship the same. However the stacking sequence of these layers is different in different modifications which leads to different structures and these are called different polytypes. As a consequence of this stacking of identical layers, the unit cell dimensions of the different polytypes are constant in two directions lying in a plane parallel to the stacked layers and differ only in the direction perpendicular to these layers. Evidently the variable dimension of the unit cell must be an integral multiple of a common unit whose value is determined by the distance between successive layers of structure. As an example silicon carbide, in which polytypism was first discovered, is known to display over 40 different polytypes. In all these modifications the hexagonal unit cell has dimensions $a = b = 3.078$Å, while c is a variable integral multiple of 2.518Å. The unit cell hights of the different polytypes range from $c \approx 5$Å in type 2H to $c \approx 1500$Å in type 594R and more in some of the unidentified types. Table 2 gives the known polytypes for silicon carbide.

Table 2. Known polytypes of SiC

	Polytype (Ramsdell notation)	Structure (Zhdanov notation)	Remarks
	A. Structures based on the "33" phase		
1.	6H	33	most common polytype
2.	33R	$(3332)_3$	
3.	$51R_a$	$[(33)_2 32]_3$	
4.	87R	$[(33)_4 32]_3$	
5.	105R	$[(33)_5 32]_3$	ordered structure
6.	141R	$[(33)_7 32]_3$	
7.	393R	$[(33)_{21} 32]_3$	
8.	21R	$(34)_3$	
9.	39R	$(3334)_3$	
10.	57R	$[(33)_2 34]_3$	structure has superposed random disorder
11.	111R	$[(33)_5 34]_3$	beautifully ordered structure
12.	16H	$(33)_2 22$	
13.	84R	$[(33)_3 3232]_3$	
14.	99R	$[(33)_4 3222]_3$	

Table 2 (*Contd.*)

	Polytype (Ramsdell notation)	Structure (Zhdanov notation)	Remarks
	B. Structures based on the 23 phase		
15.	174R	$[(33)_3 6(33)_5 4]_3$	only known polytype with a 6 in the Zhdanov symbol.
16.	36H*b*	$(33)_2 32(33)_2 34$	shows unusual extinctions on x-ray photos
17.	39H	$(33)_2 32(33)_2 3232$	
18.	15R	$(23)_3$	second commonest polytype
19.	19H	$(23)_3 22$	
20.	10H	2332	simulated hexagonal symmetry on x-ray photo
21.	75R	$[(23)_3 3232]_3$	
22.	27H	$(23)_3 3333$	
23.	90R	$[(23)_4 3322]_3$	beautifully ordered structure
24.	168R	$[(23)_{10} 33]_3$	structure not certain
	C. Structures based on the 22 phase		
25.	4H	(22)	third commonest polytype
26.	27R	$(2223)_3$	
27.	51R*b*	$[(22)_3 23]_3$	
28.	18H	$(22)_3 33$	
	D. Miscellaneous structures		
29.	β—SiC	(∞)	usually forms at lower temperatures 1800°C
30.	2H	(11)	not found in commercial SiC. Grown by special method of gaseous cracking; a=3.076Å, c=5.048 Å
31.	8H	(44)	
32.	24R	$(53)_3$	only known polytype with a 5 in its Zhdanov symbol.
	E. Polytypes with undetermined structures		
33.	24H	—	
34.	33H	—	
35.	36H$_a$	based on "33' phase	found in the same single crystal piece with 36H$_b$
36.	48H	—	
37.	54H	—	
38.	66H	—	

Table 2 (*contd.*)

	Polytype (Ramsdell notation)	Structure (Zhdanov notation)	Remarks
39.	72R	—	
40.	78H	—	
41.	120R	—	
42.	124R	—	
43.	126R	—	completely ordered structure
44.	192R	—	
45.	270R	$[(23)_{17}22]_3$ or $[(23)_{17}33]_3$	structure not certain
46.	400H or 1200R	—	
47.	594R	—	known polytype with largest unit cell c $\simeq$ 1500 Å
48.	Disordered polytypes (several)	—	x-ray photos show continuous streaks along reciprocal lattice rows parallel to c*

The property of polytypism is quite different from ordinary polymorphism in that it appears to lack the thermodynamic or phase aspect. Thermodynamically they have very nearly the same free energies and cannot be regarded as different phases of the compound. Since the different modifications have the same density and very nearly the same potential energy of configuration, neither temperature nor pressure affects their relative stabilities appreciably, and accordingly no transitions from one polytype to another have been observed.

The most striking thing about these polytypes, besides their large number of modifications, is the continued repetition and the stacking sequence of the layers, often with perfect crystalline regularity, after more than a hundred or sometimes even a thousand layers. Such enormous repeat distances, of the order of 250 to 2500Å are rare in the inanimate world but common in the crystalline viruses and other biological specimens. Well known examples are turnip yellow mosaic virus (f.c.c. $a \simeq 700$Å diamond structure) and some of the fibrous proteins (100 to 1400Å). What could be the nature of forces or the mechanism that can cause such a long periodicity in the polytypes ? No atomic forces known to physicists till now have such a long-range influence, and it is this question which has held our attention for the last few years and which has yet to be answered satisfactorily.

It might appear to the layman that this is a purely academic question of limited significance. But it is these oddities of nature which must be investigated and explained if we are to know the true nature of interatomic forces in solids. It is in these that nature has left warnings for the scientist that he is yet far from his goal of a complete understanding. The progress of science has always hinged itself on the study of such exceptions.

Various theories have been put forward from time to time to explain this remarkable phenomenon of polytypism. The early attempts were based on efforts to correlate the structure type with the contents of the impurities in silicon carbide and with the rate of crystallization from solution in cadmium iodide. There appears to be some definite correlation for the more common small period modifications, but there is no evidence of such a correlation for the long period polytypes which are being discovered in ever increasing numbers. Ramsdell and Kohn (1952) attempted to explain the formation of difficult polytypes of silicon carbide by the accretion of certain hypothetical 'polymers' with a stacking reversal inherent in their structure and stability governed by temperature. There is, however, no experimental evidence in fabour of such a mechanism.

DISLOCATION THEORY OF CRYSTAL GROWTH

The first satisfactory explanation of the mechanism of the formation of polytypic modifications had to await developments in the field of kinematics of crystals growth. The atomic theory of growth of a perfect crystal, as developed during 1940's, was unable to account for the observed rate of growth at low supersaturations. By this time it had already been recognized that real crystals are not perfect, as the theory assumed them to be, but contained imperfections of various kinds. Frank (1951) suggested that the observed growth of crystals at low supersaturations can be explained by the presence of screw dislocations and a screw dislocation theory of crystal growth was developed (Burton, Cabrera and Frank 1951). If a screw dislocation emerges on the crystal surface it raises a terminated step on the surface of the crystal, the step being anchored at one point but free to rotate round this point as crystallization proceeds. Successive stages of growth are shown in figure 1. The step is self perpetuating during the growth and thus growth at low supersaturation continues.

There are two consequences of growth by this mechanism.

1) The surface of crystal which has grown by this screw dislocation mechanism will not be a flat one as one would expect when a perfect crystal grows layer by layer On the contrary it will be a flat spiral hill the shape of which will be in accordance with the symmetry of the crystal face exhibiting it.

2) These spiral hills are molecular spiral hills. The step height of these growth spirals should be simply related to the size of the unit cells as determined by X-ray diffraction methods.

When these ideas were put forth around 1950, it was at first thought these molecular growth spirals would not be observable. However, on the (0001) faces of silicon carbide crystals, by using phase contrast microscopy, I was able to observe a wide variety of growth spirals (Verma, 1951). Similtaneously, Amelinckx (1951) also observed growth spirals on silicon carbide. Shapes of spirals originating from a single screw dislocation, or from two and more dislocations and other details were completely in accordance with theory. Figures 2, 3 and 5 illustrate a few examples.

For a precise determination of the spiral step heights which were of the order of 10Å, the sensitive technique of multiple-beam interferometry as developed by Tolansky, was employed. To our delight the step heights were found to be equal to or simply related to the X-ray unit cell size. Since then a large number of different types of crystals have been found to exhibit growth spirals with their shapes and step heights in accordance with the theory. The screw dislocation theory of crystal growth has thus been verified. For a collected account see Verma (1953).

SCREW DISLOCATION THEORY OF POLYTYPISM

An extension of this study was done on polytypes of silicon carbide with different unit cell sizes and in each polytype a correlation between their step heights and X-ray unit cell size was discovered. This led Frank (1951) to put forward a simple, pictorial, explanation of the formation of different polytypic structures of silicon carbide in terms of spiral growth round screw dislocations. According to Frank's screw dislocation theory of polytypism, the different long period polytypic structures grow from certain basic structures viz. 6H, 15R and 4H. It is believed that crystallization begins with the formation of a thin platelet of microscopic dimensions, which gets self-stressed due to non-uniform distribution of impurities or due to one of several other causes. This stress is relieved by one portion of platelet slipping past another, over a slip plane, thus creating a screw dislocation in the crystal platelet. In these basic structures if screw dislocation is created whose Burgers' Vector is an integral multiple of the parent unit cell, no new polytype is created. However, if Burgers' Vector is a non-integral multiple of the height of parent unit cell it would give rise to a new polytype. The repeat period of the resulting polytype is determined by the pitch of the screw dislocation. Screw dislocations of different Burgers' Vector would thus create different polytypes. Accordingly, the height and structure of the initial step on the crystal surface determines the formation of the polytype, the pitch of the screw becoming the length of the unit cell. The explanation is both simple and convincing.

The formation of structure series which had first been discovered by Ramsdell (1947) in silicon carbide e.g. 33R, 51R, 69R etc, is readily understood in terms of the above mechanism. Let us take the commonest type 6H structure as the structure

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PLATE 1A.

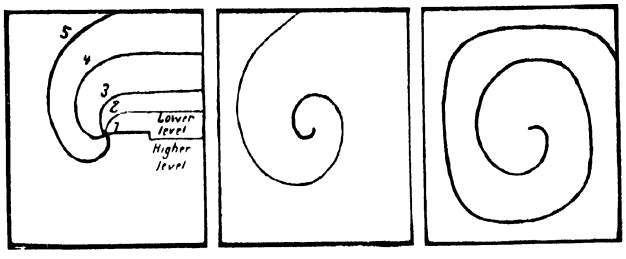

Figure 1 Successive stages of development of a growth spira

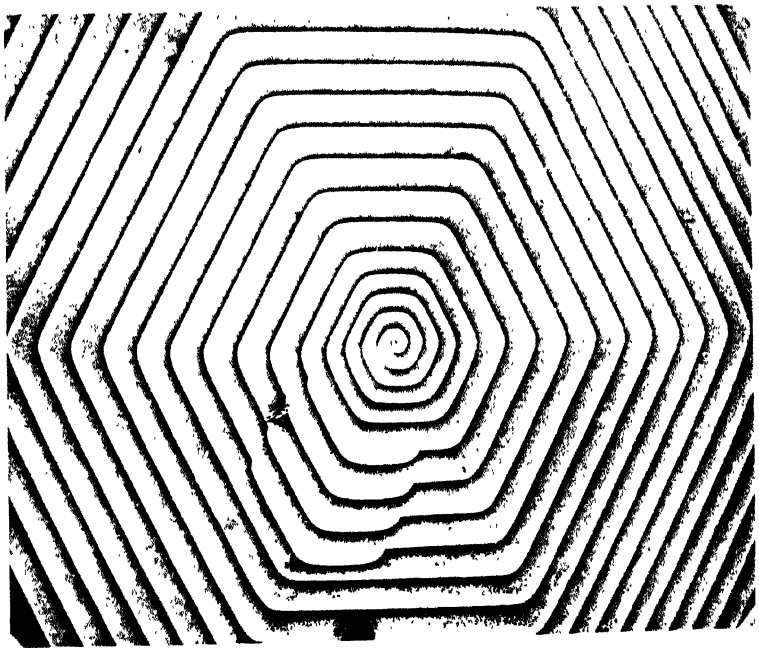

Figure 2 Phase contrast micrograph of a hexagonal spiral on SiC crystal with a step height of 165 Å. (X250)

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PLATE 1B

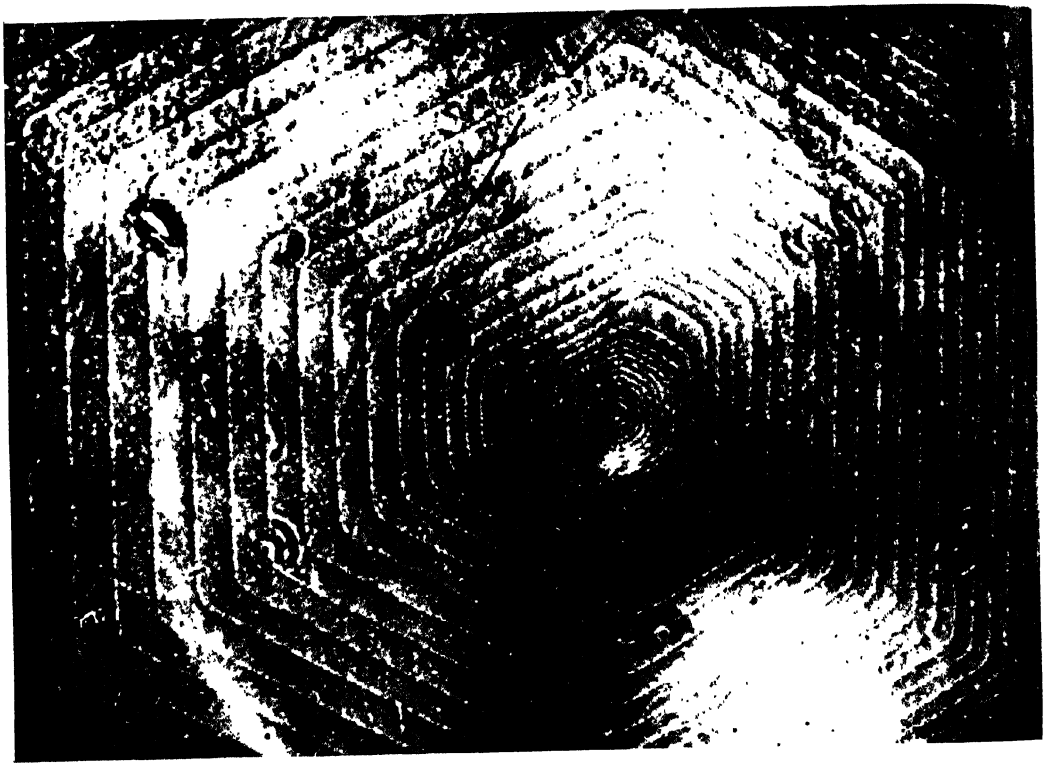

Figure 3 Phase contrast micrograph of a hexagonal spiral on SiC crystal showing closely spaced ledges at centre which may be attributed to the high supersaturation at the final stage of growth. (X200)

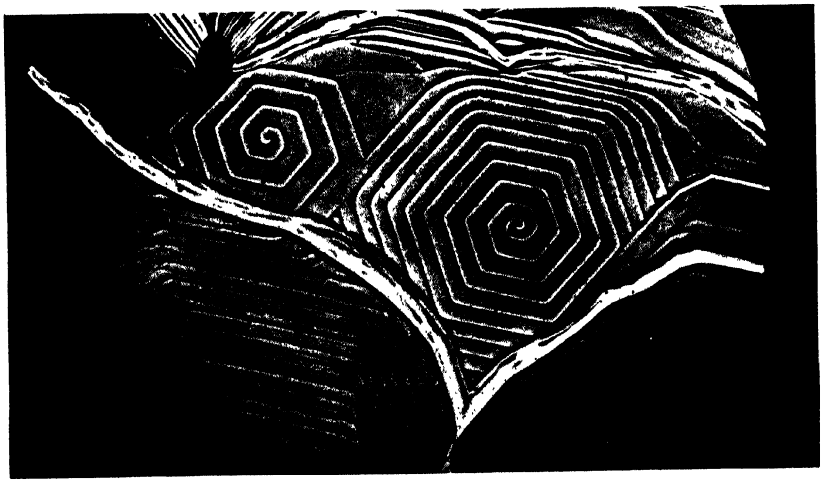

Figure 4 Phase contrast micrograph of two hexagonal spirals on SiC crystal originating from two independent dislocations of

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PLATE 2.

igure 5 Zero-layer, a-axis Weissenburg photograph of SiC type 90R (r' = 2.86 cm CuK radiaton). The lowest festoon records the 10.1 row of spots. The ten faintspots near the minimum of the festoon are, from left to right, 10. 19, 10. 16 10. 8, 10. 11. The values of successive spots differ by 3. This is an example of ordered polytype.

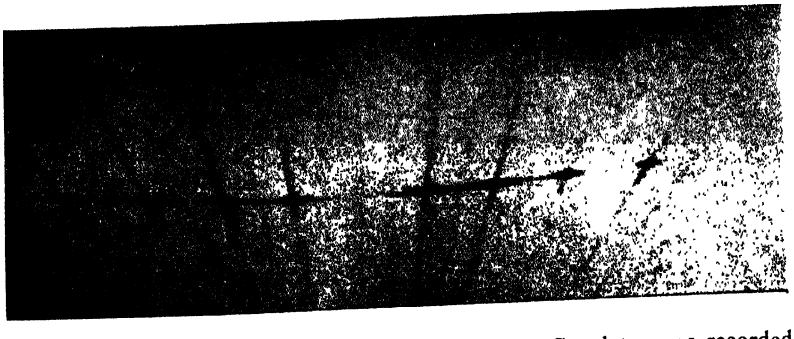

Fig re 6 The 10.1 reciprocal lattice row of a disordered SiC polytype as recorded on c-axis oscillation photograph. The disorder is revealed by the streaks joining the spots.

of the initial platelet, presumably formed at high supersaturation by the nucleation mechanism. The layer sequence for this in terms of the classical ABC layer is /ABC ACB/ABC ACB/... with the vertical bars indicating a unit cell. A screw dislocation arising in this would expose a step consisting of $6n+p$ layers where n and p are integers. When p is zero the exposed ledge has the same structure as the structure of the parent platelet and no new polytype is created. In other cases the exposed step will have a layerse quence consisting of the number of complete ABC ACB units with incomplete portion at an end like for example for $p = 5$:

BCACB(ABC ACB)$_n$ ... (i)

CACBA(BCACBA)$_n$ ... (ii)

ACBAB(CACBAB)$_n$ ... (iii)

depending upon whether the top exposed layer is a B, C or A layer. Case (i) leads to the formation of a rhombohedral lattice (Krishna and Verma 1965) since the top and bottom layer of the exposed ledge are in the same orientation, viz. B. Thus after the stack moves up by one pitch, the first and last layers will both be in orientation B. The laws of close packing do not permit two successive layers to be in the same orientation. Thus the whole stack would have to slip or be displaced horizontally in the cyclic manner $B \rightarrow C$, $C \rightarrow A$, $A \rightarrow B$ or in the anticyclic manner depending upon the controlling forces. Three such slips would have to take place in order to bring back the stack into original position, thus completing one repeat period. The height of the unit cell would therefore be three times the exposed ledge, and the structure will be a rhombohedral lattice. For $n = 1$, and $p = 5$ we get the $(6+5)\times 3 = 33$ layered rhombohedral polytype and for $n = 2, 3, \ldots$ etc. we get respectively $[(6\times 2)+5]\times 3 = 51$R, $[(6\times 3)+5]\times 3 = 69$R...etc., numbers of the series. For cases (ii) and (iii) we will get 11H, 17H, 23H, etc. polytypes. In Zhdanov notation the structure of 6H is written as (33) and of 33R, as [33 32 33 32 33 32] or for short as $[33\ 32]_3$. 51R and 69R are written as $[(3333)32]_3$ and $[(33\ 33\ 33)32]_3$ or alternatively as $[(33)_2\ 32]_3$and $[(33)_3\ 32]_3$ respectively. The explanation of the formation of the large number of polytypes belonging to the series $[(33)_n32]_3$R represented a major success of the screw dislocation theory. However, the theory was unable to account for the absence of structures belonging to other series, like $[(33)_n\ 31]_3$R and $[(33)_n\ 35]_3$R which are also theoretically possible. Mitchel (1956) has suggested that these structure series were absent because they were associated with unstable dislocation gaps in the basic structure.

EXPERIMENTAL EVIDENCE SUPPORTING THE DISLOCATION THEORY OF POLYTYPISM

There is a considerable amount of experimental evidence to support the dislocation theory of polytypism. The dislocation theory requires that the faces

of polytypic crystals should exhibit growth spirals whose step height is directly related to the corresponding dimension of the unit cell. Growth spirals had long been observed on silicon carbide. It had been felt that steps of these growth spirals were very minute and were even thought to be probably 'unimolecular' (Amelinckx, 1951). But a definite quantitative correlation between the step height of growth spirals and *c*-dimension of the unit cell was established (Verma, 1951, 1953) by applying Tolansky's multiplebeam interference method for the measurement of step height for 6H, 15R and 33R crystals. The step heights were found to be 15 ± 2Å, 12 ± 2Å, 28 ± 2Å which within experimental errors are equal to the X-ray unit cell thus establishing their correlation. It should be noted that the step is equal to the c-dimension of the hexagonal unit cell but for rhombohedral polytypes it is equal to c/3. This observation is explained Krishna and Verma, 1965) by the formation of hexagonal and rhombohedral polytypes since in the former pure screw dislocations are needed, whereas, in the latter an additional slip is needed.

Forty's (1951) observations of growth spirals in CdI_2 and the correlation of these step heights with the unit cell heights later measured by Mitchell (1956) by X-ray diffraction methods lent further support to the theory. Therefore in 1957 we felt that the phenomenon of polytypism had been satisfactorily explained.

CRITICISM OF DISLOCATION THEORY

While on the one hand, evidence in favour of dislocation theory of polytypism was mounting continuously, there were on the other hand workers who expressed doubts about several aspects of it. As early as 1951, Vand had pointed out that a single screw dislocation would give rise to a needle shaped crystal and the growth of flat platelets of silicon-carbide would require screw dislocations in other directions as well. No growth spirals have been observed on any face of silicon-carbide crystal other than (0001). The step-heights of growth spirals are often too large to be understood in terms of screw dislocations and Buckley (1952) suggested that the formation of spirals is connected with macroscopic events occurring in the vapour adjacent to the surface, at the moment of solidification. If so polytypic structure is not determined by screw dislocations at all.

JAGODZINSKI'S DISORDER THEORY OF POLYTYPISM

Jagodzinski (1954) has considered the problem on thermodynamic grounds. According to him the high energy required for the creation of a screw dislocation cannot come from the crystal structure until the crystal has grown to a considerable volume by which time it has already settled down to a certain structure. This is particularly true for screw dislocations of large Burgers' Vectors required for the formation of long period polytypes. The screw dislocation will play a role only in the later stages of growth of a crystal thereby determining its surface

structure but not its crystal structure. The correlation between Burgers' Vector of the dislocation and the unit cell dimension can be accounted for by the fact that the displaced crystal parts have a greater probability of locking up in a position of mutual fit. No new structure would thus result and the formation of different polytypic structures cannot be due to screw dislocations. Moreover since the energy required for the creation of an edge dislocation would be much less than that required for the creation of a screw dislocation of large Burgers' Vector, any order created would be destroyed.

An alternative theory has been put forth by Jagodzinski (1954). According to him the total entropy would comprise of two parts, (i) vibration entropy, (ii) configurational entropy. It is well known that configurational entropy increases with increasing disorder. In order to explain the formation of polytypic structures Jagodzinski assumes that the vibrational entropy decreases with increasing disorder. In this way another maximum can be obtained in the total entropy curve corresponding to one dimensional disordered structure. In order to visualise the role of vibration entropy in the formation of polytypes, Jagodzinski suggested a layer-transposition mechanism for their generation from the parent cubic structures. For example the formation of 6H and 15R from cubic structure is as follows where the transposed layers are underlined :

ABC ABC ABC ABC	cubic
/ABC ACB/ABC ACB	6H.
ABC ABC ABC ABC ABC	cubic
/ABC BAC AB AC BC ACB/	15R.

Similarly all other polytypic structures can be derived.

Jagodziniski determined the degree of fault order for the partially ordered polytypes, and was able to account for the partially disordered structures. The fact that there is a definite temperature-structure relationship for the small period polytypes suggests a thermodynamic basis. Growth by nucleation is in agreement with the plate-like shape of most crystals. However, according to him completely ordered long period polytypes are improbable and the longer the period the more should be the disorder since the contribution of vibration entropy to the total entropy decreases with increasing periodicity. As we shall see this is not borne out by observation nor does this theory explain the formation of structure series.

RECENT EXPERIMENTAL OBSERVATIONS AND DISCUSSION OF RESULTS

During the last few years we, therefore, undertook extensive experimental studies both of SiC and on CdI_2 to determine whether the different polytypic

structures result from growth mechanisms starting with screw dislocations or whether thermodynamic considerations are more important.

The investigation consisted of the following :

(1) To grow well developed single crystals of polytypic substances.

(2) To observe by phase contrast microscopy, the surfaces of these crystals for growth spirals.

(3) To measure accurately the spiral step heights by Tolansky's multiple —beam interferometric methods.

(4) To record X-ray diffraction spectra from the same crystal which had been examined optically.

(5) To determine the unit cell size and the detailed atomic structure of different polytypes.

Having obtained all the above experimental data about a crystal we set ourselves to interpreting it critically. If a polytypic crystal has resulted by the dislocation mechanism, the following conditions should be fulfilled :

(a) The crystal surface should exhibit a growth spiral whose step height should be correlated with the X-ray unit cell size.

(b) The polytype should be based on a basic phase. The Burgers' Vector of the polytype should be a non-integral (and not an integral multiple) of the c-dimension of the basic phase.

(c) The structures should be fully ordered with no superposed partial disorder. (see figure. 5)

Analysis of the data for a large number of silicon-carbide and cadmium iodide crystals has yielded the results summarised in the following tables :

(i) *Polytypes conforming with the dislocation theory.*

Polytype	Zhdanov symbol	
	SiC	
6H	(33)	These crystals exhibit growth spirals with step height
15R	$(23)_3$	simply correlated to the unit cell size both for hexagonal
21R	$(34)_3$	and rhomboderal polytypes.
33R	$(33\ 32)_3$	
	CdI_2 :	
2H	(11)	The spiral step height was an integral multiple of the c-dimension of the 2H-type only.

Conclusion : Growth of the above SiC polytypes is completely explained by dislocation mechanism. But in CdI_2 no correlation was observed for polytypes other than 2H.

(ii) *Polytypes expected on dislocation mechanism but not showing growth spirals*

SiC:

Polytype	Zhdanov symbol	
57R	$[(33)_2\ 34]_3$	Formation of these polytypes is readily explained on
111R	$[(33)_5\ 34]_3$	dislocation mechanism but there is no evidence of a dislocation since they do not exhibit growth spirals.

CdI_2

26H	$(22)_6\ 11$	Ditto

Conclusion : Either these polytypes have not resulted by spiral growth or the growth spiral was wiped off in the later stages of growth.

(iii) *Polytypes not expected on dislocation mechanism but exhibiting growth spirals.*

SiC

54H	Both are based on 6H phase. Since the unit cells are
66H	multiple of c-dimension of the basic structure, these cannot result from dislocations yet these show growth spirals with step height correlated with the unit cell size.
126R	The correlated spiral step height gives evidence of growth by dislocation mechanism but its structure $[(33)_3(43)_2\ 32\ 23]_3$ is at variance.

CdI_2 :

28H	Its Zhdanov symbol is $(22)_6\ 1111$. It is based on 4H phase but its unit cell is exactly 7 times c-dimension of the 4H. The (0001) face shows a single spiral.

Conclusion : These polytypes do not appear to have resulted from the spiral growth which they exhibit.

(iv) *Polytypes not expected on dislocation and also not showing growth spiral.*

SiC :

36H	Based on 6Hwith structure $(33)_2 34 (33)_2 32$.
90R	Based on 15R with structure $[(23)_4 3322]_3$ (see figure 5)

CdI_2 :

22H	Based on 2H with structure $(11)_5\ 2211\ \ 2211$
26H	Based on 2H with structure $[2(11)_2]_3\ 2(11)_3$

Conclusion: These polytypes could not have resulted from the respective basic phases since the Burgers' Vector of the resultant polytypes is an integral multiple of the c-dimension of the basic phase. These also do not show growth spirals.

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